

# Is acetylene essential for carbon dust formation?

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25 April 2013

## ABSTRACT

We have carried out an investigation of the chemical evolution of gas in different carbon-rich circumstellar environments. Previous studies have tended to invoke terrestrial flame chemistries, based on acetylene ( $\text{C}_2\text{H}_2$ ) combustion to model the formation of carbon dust, via Polycyclic Aromatic Hydrocarbons (PAHs). In this work we pay careful attention to the accurate calculation of the molecular photoreaction rate coefficients to ascertain whether there is a universal formation mechanism for carbon dust in strongly irradiated astrophysical environments. A large number of possible chemical channels may exist for the formation of PAHs, so we have concentrated on the viability of the formation of the smallest building block species,  $\text{C}_2\text{H}_2$ , in a variety of carbon-rich stellar outflows.  $\text{C}_2\text{H}_2$  is very sensitive to dissociation by UV radiation. This sensitivity is tested, using models of the time-dependent chemistry. We find that  $\text{C}_2\text{H}_2$  formation is sensitive to some of the physical parameters and that in some known sources of dust-formation it can never attain appreciable abundances. Therefore multiple (and currently ill-defined) dust-formation channels must exist.

**Key words:** astrochemistry - molecular processes - stars: AGB and post-AGB - dust, extinction - ISM: molecules

## 1 INTRODUCTION

The observational properties of dust and the physical consequences of its presence in the interstellar medium and extremely well-known and well-documented (Draine 2003). However its composition, structure and size-distribution are still subjects of much discussion. Even though there are no direct samples of interstellar dust, carbonaceous dust deposits found in meteorites give us an indication of what structure and composition we might expect. These grains consist of a core of microcrystalline aromatic moieties surrounded by a crystalline graphite mantle (Tielens 1997). Significantly, the precise chemical kinetic pathways leading to the (relatively simple) case of carbon-dust formation are almost entirely speculative.

The recent observations of higher than expected dust masses around high redshift quasars (Dwek, Galliano & Jones 2007; Bertoldi et al. 2003) and local supernovae (Matsuura et al. 2011), has caused a resurgence of interest in the issues of dust formation mechanisms and efficiencies. In the local universe, dust is observed mainly in two environments: dense interstellar clouds and circumstellar media. The main sources of interstellar dust are believed to be evolved red giants, novae and supernovae (Dwek 2004; Salpeter 1977; see Tielens 2008 for a review). There are thus two questions that we address in this paper: (i) what is the chemical pathway for the formation of macromolecular species that leads to the formation of dust nucleation sites?, and (ii) what range of physical parameters determine the viability of these pathways?

For the sake of (relative) simplicity we limit our discussion to the formation of carbon dust in carbon-rich circumstellar environments, making the simplifying assumption that the oxygen is completely locked up in the relatively inert form of CO. In such an environment the C:O ratio - 1 is thus a crucial parameter. However, it should be noted (see below) that this usually-assumed approximation has been challenged by relatively recent observational and modelling efforts.

Some of the earliest attempts at modelling carbon dust formation concentrated on novae, some of which are seen to produce very optically thick (carbon) dust shells on timescales of days. Rawlings (1988) developed a proto-PDR model of the chemistry in novae ejectae, and found that molecule formation requires the presence of  $\text{H}_2$  and carbon neutrality (CI). The presence of  $\text{C}^+$  (and the carbon ionization continuum) inhibits molecule formation. Chemical equilibrium is established very fast (within  $\sim 10$ s). Rawlings & Williams (1989), hereafter RW89, extended this and proposed a non-LTE chemical kinetic model of (carbon) dust formation in novae ejectae which proceeds via a limited hydrocarbon chemistry - totally dominated by the photophysics, and requiring all oxygen to be locked up in CO. This latter finding has been challenged - both by the observations that suggest that carbon dust is formed in oxygen rich ( $\text{O}>\text{C}$ ) environments (e.g. Andreä, Drechsel & Starrfield 1994) - and also models of the chemistry in nova outflows (Pontefract & Rawlings 2004). In these models  $\text{C}_2$  (for which the more significant of the two pre-dissociation bands is shielded against photodissociation in a CI region) is the key building block species, rather than  $\text{C}_2\text{H}_2$  which is susceptible to photodissociation. As such, nucleation of dust was

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found to be possible only in a CI region, but requires some source of ionization to drive the chemistry.

Pontefract & Rawlings (2004) extended the work by RW89 by including oxygen and nitrogen chemistry and updated the photoreaction rates. Surprisingly, they found that the overall chemistry is not as dependent on the photochemistry as earlier studies had suggested and that carbon dust could be formed even when all of the oxygen is not ‘locked’ in CO. The work highlighted that CN, CO and C<sub>2</sub> are key molecular species in the formation pathways of larger species. Although C<sub>2</sub>H<sub>2</sub> was included its chemistry was not closely scrutinised.

More generally, it has been proposed that Polycyclic Aromatic Hydrocarbon molecules (PAHs) are key intermediates in carbon dust formation and act as nucleation sites for dust grains (Helling et al. 1996; Cherchneff, Barker & Tielens 1992). This inferred link is due to the close relationship between the molecular structure of PAHs and the carbon structure of graphite. Also, observations of the far-IR continuum due to carbon dust are accompanied by strong PAH features (Tielens 2008). However, some caution should be exercised with the interpretation of these features. For example, PAH (and/or hydrogenated amorphous carbon) emission is also detected in some carbon-dust producing novae but in all cases it is only seen well *after* dust formation and in an environment when it would be susceptible to photodissociation. This indicates that - for novae at least - the PAHs are transitory products of dust destruction, rather than intermediates to dust formation (Evans & Rawlings 2008).

Gail & Sedlmayr (1987) proposed chemical mechanisms required to form PAH molecules in stellar winds. The acetylene molecule (C<sub>2</sub>H<sub>2</sub>) was found to be crucial in the formation pathway. An important contribution came from Frenklach & Feigelson (1989), hereafter (FF89). They investigated a mechanism of PAH formation, using a chemical kinetic approach. The chemistry network was based on soot production in terrestrial hydrocarbon flames, which they applied to astrophysical conditions, i.e. much lower pressure and densities. They confirmed that the complex network of chemical reactions can essentially be described by a sequence of hydrogen abstraction followed by acetylene addition.

Acetylene does not possess a permanent dipole moment and so does not have a rotational spectrum observable at radio wavelengths. It is therefore somewhat elusive; - detections rely on rovibrational transitions, observable in the mid-infrared. For this reason, detections tend to be limited to the warm gas (~100 – 1000K) along the lines of sight towards young stellar objects (e.g. Boonman et al. 2003). There is also strong evidence for the presence of C<sub>2</sub>H<sub>2</sub> in evolved carbon stars; the most well known of which - IRC+10216 - exhibits a forest of C<sub>2</sub>H<sub>2</sub> lines in the 11–14μm window (Fonfría et al. 2008). Indeed, after H<sub>2</sub> and CO, C<sub>2</sub>H<sub>2</sub> is determined to be the most abundant species in the gas - with a fractional abundance of ~8 × 10<sup>-5</sup> - although this is primarily detected *outside* the dust-formation zone and so is not necessarily associated with the dust-formation process. There may even be some evidence of C<sub>2</sub>H<sub>2</sub> freeze-out into icy mantles at larger radii in IRC+10216, and an icy mantle-based origin for interstellar C<sub>2</sub>H<sub>2</sub> is strongly suggested by Spitzer observations of the correlation between C<sub>2</sub>H<sub>2</sub> and gas-phase CO<sub>2</sub> towards Cepheus A East (Sonnentrucker, González-Alfonso & Neufeld 2007).

Cherchneff, Barker & Tielens (1992) addressed the issue of PAH chemistry and dust formation in the carbon-rich envelopes of late AGB stars; driven by stellar pulsations and (strong, density enhancing) shocks. Although extremely dense, the gas is much cooler and not subject to the intense FUV radiation field that is

present in a nova, so the chemical model was based on a terrestrial neutral gas acetylenic-burning soot chemistry. In such environments the carbon budget is largely split between CO and C<sub>2</sub>H<sub>2</sub>. The chemistry was largely based on well-studied flame chemistries (eg. FF89), expanded and augmented to include free radicals. It was found that C<sub>2</sub>H<sub>2</sub> is the key species in macro-molecular growth and (especially) ring closure/cyclization to form aromatic hydrocarbon rings, as well as the polymerization to multiple ring PAHs. The formation of the first aromatic ring is often recognised as the main ‘bottleneck’ in macro-molecular growth/dust nucleation. In this, as in later studies (e.g. Cherchneff & Cau 1999), ring closure was found to proceed following reactions of two propargyl radicals (C<sub>3</sub>H<sub>3</sub>) or via a lesser channel involving reaction of acetylene with 1,3 butadiyne (C<sub>4</sub>H<sub>2</sub>) (e.g. see Figs. 3 & 4 in that paper). In either case C<sub>2</sub>H<sub>2</sub> initiates the chemistry. Reaction networks need to include both two-body and three-body reactions, but did not include photoreactions, or an ion-molecule chemistry. Although they were able to identify the presence of a temperature window (900–1100K) in which the formation of PAHs is possible, the formation efficiency is too low - possibly due to the lack of inclusion of the effects of a local UV radiation field and/or an ion-molecule chemistry.

Considering a different class of object Woods et al. (2002) modelled the formation of benzene (C<sub>6</sub>H<sub>6</sub>) in a protoplanetary nebula (CRL618) where the chemistry is characterised by high densities, temperatures and ionization rates - although photoreactions were significantly inhibited throughout the molecule-formation zone due to the assumed presence of dust. This chemistry is somewhat different to the Cherchneff et al. schemes due to the presence of a degree of ionization and an efficient ion-molecule chemistry. However, even in these conditions, C<sub>2</sub>H<sub>2</sub> plays a crucial role - mainly through the initiating reaction of



All of the above models and reaction schemes have made extremely simplistic assumptions about the radiation field and the photoreaction rates; either by only considering the chemistry in low luminosity environments (or external to an optically thick dust-formation zone) - in which case they are ignored, or by simply ‘scaling up’ interstellar photoreaction rates in a way that does not properly take into account the specific nature of the radiation field and/or the significance of ionization continua. The overall aim of this work is therefore to include an ion-molecule chemistry and a careful recalculation of the photoreaction rates using local radiation fields and accurate cross-sectional data to re-assess the viability of C<sub>2</sub>H<sub>2</sub> formation in a variety of carbon-rich circumstellar environments. As C<sub>2</sub>H<sub>2</sub> is fundamental to the formation of PAH molecules, we try to determine if the amount of C<sub>2</sub>H<sub>2</sub> produced in carbon rich AGB and nova environments is enough to seed dust formation. We use a specially adapted chemical network for high temperatures and densities, paying particular attention to a more accurate account of the photochemistry involved in non-interstellar conditions, which (as explained above) previously had been highly over-simplified. We investigate a broad range of dust-forming objects which includes carbon stars with effective temperatures higher than AGB stars (e.g. CH subgiants), novae and R Coronae Borealis stars. By doing this we aim to establish the range of parameter space within which effective C<sub>2</sub>H<sub>2</sub> formation (and by inference PAH formation) is possible.

In section §2, we describe the model that was implemented. Section §3 specifies the physical and chemical parameters used for the three different carbon rich circumstellar environments that we

have modelled. We describe the results and analysis in section §4. Finally, in section §5 we summarise our results and their implications.

## 2 THE MODEL

The nucleation sites for dust grain formation are formed in the gas phase in a cooling, expanding atmosphere, such as in the outflow from a red giant (Cadwell et al. 1994). Therefore if PAHs are the key intermediate molecules to carbonaceous dust they should also be formed in the stellar winds that feed the circumstellar environment. We therefore model the time-dependent chemistry that occurs in an appropriately located gas parcel. This will be the part of the envelope whose temperature lies within the range that is appropriate for dust formation - corresponding to the ‘condensation radius’ in previous studies (eg. Clayton & Wickramasinghe 1976).

As explained above, the main chemical pathway to form a PAH molecule starts with the polymerization of  $C_2H_2$  (Gail & Sedlmayr 1987) and we therefore identify acetylene as being the key molecule in the formation of larger species, such as PAHs. We investigate the viability of acetylene formation as being the controlling factor in the formation of dust nucleation sites via PAHs as intermediate macro-molecules.

The gas in stellar outflows is dense ( $n > 10^9 \text{ cm}^{-3}$ ) and warm ( $T > 1000 \text{ K}$ ), so that (providing the gas is not *too* hot, such that bond-breaking, collisional dissociation reactions can occur), molecules can be formed efficiently and quickly. As the gas expands and its density falls, the chemical reaction rates are quenched. However, the geometrical dilution timescale is typically many orders of magnitude larger than the chemical kinetic timescale (Rawlings 1988) and this is not a critical factor in determining the dust-formation efficiency. Despite the possible presence of shocks etc. - and although the gas is very far from thermal equilibrium, the characteristic timescale of the outflow is much larger than the chemical kinetic timescale. We therefore assume that both the circumstellar environment and the stellar wind are spherically symmetric around the star and that the physical conditions (density, temperature, radiation dilution factor etc.) are not time dependent and remain constant.

The chemistry is evolved to chemical equilibrium which, as argued above, occurs on a timescale that is very much shorter than that for which changes in the physical conditions occur. In practice, equilibrium was determined from the requirement that the abundances of all species changed by  $< 1\%$  on any time step and typically was achieved on timescales of seconds. We have investigated the sensitivity of the equilibrium abundances to the physical conditions. The key free parameters that we have varied are: the total abundances of the elements, the photospheric temperature of the star, the density and the temperature of the gas. Other parameters, such as the dilution factor for the radiation field, are taken to be defined by the observed location of dust formation. The elemental abundances are given in Table 4. The cosmic ray ionization rate is set to  $10^{-17} \text{ s}^{-1}$ , which is representative of the assumed galactic background rate (Dalgarno 2006).

### 2.1 The Chemistry

The chemical network includes 1537 reactions between 102 gas-phase species involving 8 elements (H, He, C, N, O, S, Na and Si). These are listed in Table 1.

The chemical complexity of the reactants was limited as we

**Table 1.** Chemical Species

H, H <sub>2</sub> , H <sup>+</sup> , H <sup>-</sup> , H <sub>2</sub> <sup>+</sup> , H <sub>3</sub> <sup>+</sup>
C, C <sup>+</sup> , C <sup>-</sup> , CO, CO <sup>+</sup> , CH, CH <sup>+</sup> , CH <sub>2</sub> , CH <sub>2</sub> <sup>+</sup> , CH <sub>3</sub> , CH <sub>3</sub> <sup>+</sup>
CH <sub>4</sub> , CH <sub>4</sub> <sup>+</sup> , C <sub>2</sub> , C <sub>2</sub> <sup>+</sup> , C <sub>2</sub> H, C <sub>2</sub> H <sup>+</sup> , C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>2</sub> <sup>+</sup>
N, N <sup>+</sup> , NH, NH <sup>+</sup> , NH <sub>2</sub> , NH <sub>2</sub> <sup>+</sup> , NH <sub>3</sub> , NH <sub>3</sub> <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , N <sub>2</sub> , N <sub>2</sub> <sup>+</sup> , N <sub>2</sub> H <sup>+</sup>
O, O <sup>+</sup> , O <sup>-</sup> , O <sub>2</sub> , O <sub>2</sub> <sup>+</sup> , OH, OH <sup>-</sup> , OH <sup>+</sup> , H <sub>2</sub> O, H <sub>2</sub> O <sup>+</sup> , H <sub>3</sub> O <sup>+</sup>
HCO, HCO <sup>+</sup> , H <sub>2</sub> CO, H <sub>2</sub> CO <sup>+</sup> , CO <sub>2</sub> , CO <sub>2</sub> <sup>+</sup>
CN, CN <sup>+</sup> , CN <sup>-</sup> , HCN, HCN <sup>+</sup> , HNC, HCNH <sup>+</sup>
NO, NO <sup>+</sup> , HNO, HNO <sup>+</sup> , NO <sub>2</sub> , NO <sub>2</sub> <sup>+</sup> , OCN
He, He <sup>+</sup> , HeH <sup>+</sup> , Na, Na <sup>+</sup> , e <sup>-</sup>
S, S <sup>+</sup> , S <sup>-</sup> , HS, HS <sup>+</sup> , H <sub>2</sub> S, H <sub>2</sub> S <sup>+</sup> , H <sub>3</sub> S <sup>+</sup>
CS, CS <sup>+</sup> , HCS, HCS <sup>+</sup> , H <sub>2</sub> CS <sup>+</sup> , SO, SO <sup>+</sup> , SO <sub>2</sub> , SO <sub>2</sub> <sup>+</sup> , OCS, OCS <sup>+</sup>
NS, Si, Si <sup>+</sup> , SiH, SiH <sup>+</sup> , SiH <sub>2</sub> <sup>+</sup> , SiO, SiO <sup>+</sup> , SiOH <sup>+</sup> , SiO <sub>2</sub>

**Table 2.** Main formation reactions of  $C_2H_2$ , rates from Woodall et al. (2007)

	Reaction	Reaction rate
1	$CH_2 + CH_2 \rightarrow C_2H_2 + 2H$	$k_1 = 1.80 \times 10^{-10} e^{-400K/T}$
2	$CH_2 + CH_2 \rightarrow C_2H_2 + H_2$	$k_2 = 2.63 \times 10^{-9} e^{-6013K/T}$
3	$H^- + C_2H \rightarrow C_2H_2 + e^-$	$k_3 = 1.00 \times 10^{-9}$
4	$C^- + CH_2 \rightarrow C_2H_2 + e^-$	$k_4 = 5.00 \times 10^{-10}$
5	$C + CH_3 \rightarrow C_2H_2 + e^-$	$k_5 = 1.00 \times 10^{-10}$

only concentrate on the initiating steps in the formation of larger molecular species.

The ratefile is an adapted set of reactions, applicable to high densities, high temperatures and intense radiation fields. Many of the reactions and rate coefficients ( $k_i$ ) were taken from the UMIST database for Astrochemistry (Woodall et al. 2007) where the formulation for the rate coefficients is valid in the operative temperature range. Additional data was taken from databases that are relevant to high temperature/high density environments (e.g. Rawlings, Drew & Barlow 1993; Lim, Raga, Rawlings & Williams 2002; Pontefract & Rawlings 2004, etc.). Although the densities are very much larger than those applicable to interstellar studies, they are not so high ( $\geq 10^{12} \text{ cm}^{-3}$ ) that three-body reactions need to be taken into account.

Reaction types that are included in the chemistry are: charge transfer, ion-molecule, radiative association, neutral exchanges, radiative recombination, dissociative recombination and negative ion reactions. Reactions which are particularly significant in addition to those applicable to interstellar clouds are neutral-neutral reactions, reactions with significant activation energy barriers, and reactions between ro-vibrationally excited species, due to the high temperatures that exist in circumstellar outflows.

The main formation and destruction reactions for  $C_2H_2$  are given in Tables 2 and 3.

#### 2.1.1 Photoreactions

In circumstellar environments, irradiated by the central star, the UV radiation field is typically very much stronger and has quite a different spectral shape to that which pertains in the interstellar medium. It is therefore important that we pay particular attention to the correct evaluation of the photo-reaction rate coefficients: The rates for all photodissociation, photoionisation and photodetachment reactions are calculated *ab initio*.

In these conditions, the key factor in determining the viability

**Table 3.** Main destruction reactions of  $C_2H_2$ , rates from Woodall et al. (2007)

	Reaction	Reaction rate
6	$C + C_2H_2 \rightarrow C_3H + H$	$k_6 = 1.45 \times 10^{-10} \left(\frac{T}{300}\right)^{-0.12}$
7	$C + C_2H_2 \rightarrow C_3 + H_2$	$k_7 = 1.45 \times 10^{-10} \left(\frac{T}{300}\right)^{-0.12}$
8	$H^+ + C_2H_2 \rightarrow C_2H_2^+ + H$	$k_8 = 5.40 \times 10^{-10}$
9	$H + C_2H_2 \rightarrow C_2H + H_2$	$k_9 = 3.80 \times 10^{-10} e^{-\frac{13634}{T}}$
10	$O + C_2H_2 \rightarrow CO + CH_2$	$k_{10} = 8.39 \times 10^{-12} \left(\frac{T}{300}\right)^{1.03} e^{-\frac{1197}{T}}$
11	$O + C_2H_2 \rightarrow C_2H + OH$	$k_{11} = 5.30 \times 10^{-9} e^{-\frac{8520}{T}}$
12	$He^+ + C_2H_2 \rightarrow CH^+ + CH + He$	$k_{12} = 7.70 \times 10^{-10}$
13	$He^+ + C_2H_2 \rightarrow C_2^+ + He + H_2$	$k_{13} = 1.61 \times 10^{-9}$
14	$He^+ + C_2H_2 \rightarrow C_2H^+ + He + H$	$k_{14} = 8.75 \times 10^{-10}$
15	$He^+ + C_2H_2 \rightarrow C_2H_2^+ + He$	$k_{15} = 2.54 \times 10^{-10}$
16	$C^+ + C_2H_2 \rightarrow C_3H^+ + H$	$k_{16} = 2.20 \times 10^{-9}$
17	$S^+ + C_2H_2 \rightarrow HC_2S^+ + H$	$k_{17} = 9.50 \times 10^{-10}$
18	$Si^+ + C_2H_2 \rightarrow SiC_2H^+ + H$	$k_{18} = 1.30 \times 10^{-10} \left(\frac{T}{300}\right)^{-0.71} e^{-\frac{29}{T}}$
19	$Si^+ + C_2H_2 \rightarrow SiC_2H_2^+ + \text{photon}$	$k_{19} = 2.50 \times 10^{-10}$
20	$Si + C_2H_2 \rightarrow SiC_2 + H_2$	$k_{20} = 1.00 \times 10^{-13} \left(\frac{T}{300}\right)^{-1.00}$

ity of any chemical kinetic pathway that leads to dust-formation is therefore the stability of the intermediates against photodissociation/photoionisation by the stellar radiation field.

The calculation of the photorates by a time-dependent non-interstellar radiation field in an expanding atmosphere is a non-trivial task. There are two components to the calculation of the photoreaction rate-coefficients in the local radiation field:

- (i) a basic ‘photospheric’ rate, calculated for the specific photoreaction and radiation field
- (ii) a time-dependent geometrical dilution, due to the expansion of the wind

In earlier models, and for the sake of simplicity, photoreaction rates were calculated by scaling the unshielded interstellar photorates by a ratio of the stellar flux to that of the interstellar radiation field, either by a single scaling factor, or by a value appropriate to a single characteristic wavelength for each reaction in question (Rawlings 1988). In this study we use a more accurate approach that can encompass the variety of situations that we wish to investigate: Photoreactions are calculated by fully integrating the known cross-sections and oscillator strengths (for line transitions) over the specified radiation field. Following van Dishoeck (1988) we treat the contributions to the photodissociation rate arising from continuous absorption and those arising from absorption in discrete transitions as separable. These can be written as

$$k_{pd}^{cont} = \int \sigma(\lambda) I(\lambda) d\lambda s^{-1} \quad (1)$$

and

$$k_{pd}^{line} = \frac{\pi e^2}{mc^2} \lambda_{ul}^2 f_{ul} \eta_u x_l I(\lambda_{ul}) s^{-1} \quad (2)$$

respectively, where  $k$  is the photoreaction rate coefficient,  $\lambda$  is the wavelength,  $I_\lambda$  is the flux,  $\sigma(\lambda)$  is the cross-section for the reaction,  $f_{ul}$  is the oscillator strength and the other symbols have their usual meanings. Photoreaction cross-sectional data and oscillator strengths were taken from a variety of sources (e.g. van Dishoeck 1988; Rawlings, Drew & Barlow 1993) as described in Rollins & Rawlings (2012). We assume that the gas is within the carbon-neutral zone (equivalent to being behind the photodissociation region: As was shown in Rawlings (1988), complex chemistries are unsustainable in CII regions). We therefore assume

that  $H_2$  and  $CO$  are fully self-shielding and that carbon photoionization is effectively suppressed. The lower limit of the integral in equation 1 is therefore set to the ionization threshold for C I (1102Å).

This study is too generalised to consider the radiation fields of individual sources so we instead opt to characterise the radiation field by that of an (appropriately diluted) single temperature black-body ( $T_{BB}$ ). In addition, as we have investigated a wide range of  $T_{BB}$  which may also be time-dependent, we have utilised a parametric fit to the dependence of the photoreaction rates to  $T_{BB}$ . Thus, after calculating the photospheric rates for several values of  $T_{BB}$  we fit a simple quadratic to the logarithm of the rates:

$$\log(k) = a + b \cdot \log T_{BB} + c \cdot (\log T_{BB})^2 \quad (3)$$

where the coefficients  $a, b$  and  $c$  are specific to each reaction and are defined for a certain temperature range. The ranges used are as specified in Table 4.

For the geometrical dilution we assume simple spherical symmetry, in which case, at a distance  $R$  from the star, the the dilution factor is given by

$$W = \left(\frac{R_\star}{2R}\right)^2 \quad R \gg R_\star, \quad (4)$$

where  $R_\star$  is the photospheric radius of the star.

To ascertain the viability of the efficient formation of  $C_2H_2$ , we will need to study the chemistry in the vicinity of the ‘condensation radius’ where dust grains start to form. In the case of AGB envelopes, this is also where outflow acceleration due to radiation pressure on newly formed dust grains starts. For AGB winds, the radius of condensation,  $R_c$ , is given by Cherchneff, Barker & Tielens (1992);

$$R_c = R_\star \left( 1 - \left[ 1 - 2 \left( \frac{T_{gas}}{T_{phot}} \right)^{4.85} \right]^2 \right)^{-0.5}. \quad (5)$$

Substituting this into equation (4), the dilution factor becomes

$$W = \frac{1}{4} \left\{ 1.0 - \left[ 1.0 - 2.0 \left( \frac{T_{gas}}{T_{phot}} \right)^{4.85} \right]^2 \right\}. \quad (6)$$

which is only dependent on the ratio of the temperature of the pho-



tosphere ( $T_{\text{phot}}$ ) to that in the gas ( $T_{\text{gas}}$ ). In the case of the AGB winds, the temperature of the gas parcel is set at 1000K, which is the midpoint of the temperature window for PAH formation (900-1100 K) found by Cherchneff, Barker & Tielens (1992).

Finally, we include a (small) contribution to the photorate deriving from the local internally generated UV field induced by cosmic ray ionizations (Prasad & Tarafdar 1983; Gredel et al. 1989).

### 3 PHYSICAL AND CHEMICAL PARAMETERS

We have investigated four different carbon-rich (C>O) astrophysical environments. We have studied acetylene formation in the outflows from:

- (i) Thermally pulsing asymptotic giant branch (AGB) stars,
- (ii) Novae,
- (iii) G/K-type Carbon stars, and
- (iv) R Coronae Borealis-type stars.

The physical conditions are quite different in these four classes of objects, yet they are each known to be prolific sources of carbon dust.

Firstly, we have extended the work of Cherchneff, Barker & Tielens (1992), which modelled PAH formation in the post-shock gas in thermally pulsing asymptotic giant branch (AGB) stars. These are well known dust production sites. Including a more complete photochemistry has allowed us to determine more accurately the stability of  $\text{C}_2\text{H}_2$  in this environment. We have applied our model to examine the viability of PAH formation in the ejecta around novae, some of which (but not all) are also known to be efficient dust-producers. We have also investigated the outflows from stars that are somewhat hotter than AGB stars, so that we can ascertain the possibility of soot chemistries operating in these circumstellar environments. Finally, we have modelled the conditions required for acetylene-driven dust formation in R Coronae Borealis (R Cor Bor) stars, which are well-known to be prolific dust-producers. The initial conditions selected for each of these four scenarios are discussed below.

There are considerable variations (and uncertainties) in the observationally inferred elemental abundances for each source type. However, the C:O ratio is a key parameter. This determines the efficiency of the hydrocarbon chemistry and, hence (whatever reaction pathway is followed) the viability of carbon dust formation. To effect the requisite variations in the C:O ratio we have adopted cosmic abundance values for all elements other than carbon; 0.85,  $6.0 \times 10^{-5}$ ,  $4.6 \times 10^{-4}$ ,  $1.4 \times 10^{-5}$ ,  $3.5 \times 10^{-5}$  and  $3.2 \times 10^{-5}$  for He, N, O, S, Na and Si respectively. The abundance of carbon is then varied to give the (observed) C:O ratio as specified in Table 4.

#### 3.1 Case I: AGB STARS

High carbon-oxygen ratios ( $> 2$ ) are unlikely in the Galaxy (although common in the Large Magellanic Cloud) and are excluded. Lower ratios of  $\text{C} : \text{O} \sim 1.5$  are expected for most carbon stars (Bergeat, Knapik & Rutily 2001). Lambert et al. (1988) found slightly subsolar values for the oxygen and nitrogen abundances in AGB stars, but our approximation of using solar abundances is essentially valid. This is consistent with the abundances used by Cherchneff, Barker & Tielens (1992) to model an AGB star that is similar to the well-known source IRC+10216. We can therefore compare our results to Cherchneff, Barker & Tielens (1992) and distinguish the effects of including a complete photochemistry.

In a study of 390 carbon rich stars by Bergeat, Knapik & Rutily (2001), the highest effective temperature evaluated was  $3870 \pm 1080$  K. We have therefore investigated photospheric temperatures in the range  $T=1500\text{-}3500\text{K}$ . The initial conditions and parameter ranges that we consequently adopt for AGB outflows are given in Table 4.

#### 3.2 Case II: NOVAE

It has long been established that dust is sometimes formed, rapidly and efficiently, in nova outflows (e.g. Gallagher 1977). In the most extreme circumstances, a steep decrease in the visual emission occurs, accompanied by a strong rise in thermal infrared emission - as an optically thick dust shell is formed (Clayton & Wickramasinghe 1976). Following Rawlings (1988), we adopt the following relations between the physical parameters:

$$\Delta m_V = \dot{m}_V \times t_0, \quad (7)$$

$$L_{\text{nova}} = 1.036 \times 10^6 \times \dot{m}_V, \quad (8)$$

$$r_{\text{phot}} \sim 9.97 \times 10^9 \times L_{\text{nova}}, \quad (9)$$

$$T_{\text{phot}} = 15280 \times 10^{\left(\frac{\Delta m_V}{7.5}\right)}, \quad (10)$$

where  $\dot{m}_V$  is the rate of magnitude decline in the optical,  $r_{\text{phot}}$  is the initial photospheric radius,  $L_{\text{nova}}$  is the nova luminosity and  $t_0$  is the number of days post outburst.

The values for the rate of visual decline from maximum ( $\dot{m}_V = 0.03 \text{ mag d}^{-1}$ ) and time at start of calculation ( $t_0 = 30$  days post outburst) were adopted following Rawlings & Williams (1989). Novae can be classed by the time taken for a nova to diminish by 2 magnitudes below maximum visual brightness. Generally, ‘slower’ novae (i.e. those with smaller values of  $\dot{m}_V$ ) are more effective at producing optically thick shells of carbon dust. Parameters for a typical dust-producing nova are given in Table 5 and are used in our model. The parameter range investigated and initial conditions are given in the Table 4. The fractional abundance of carbon is much higher than in the case of AGB stars (Rawlings & Williams 1989). This is due to the thermonuclear processing of the gas and dredge-up of white dwarf material that occurs following the thermonuclear runaway that drives the nova outburst. The upper limit of density was inferred from observations (e.g. Rawlings 1988).

#### 3.3 Case III: CARBON STARS IN SPECTRAL CLASS G-K

We investigate stars with photospheric temperatures in the range 3750–6000K. Low mass main sequence stars are not likely to have a high C:O ratio. However, CH subgiants are low luminosity peculiar giants, which have a high C:O ratio in their atmosphere as a result of mass transfer from an evolved companion (Smith, Coleman & Lambert 1993). The upper limit of C:O observed in these stars is 1.5 (Luck & Bond 1982). The parameter ranges chosen to represent these objects are given in Table 4. We have optimised the parameters for dust production by only considering the highest values possible for the C:O ratio and the gas density.

#### 3.4 Case IV: R CORONAE BOREALIS STARS

R Coronae Borealis stars (RCB’s) are yellow supergiants which are hydrogen deficient and carbon rich. These stars show irregular declines in visual brightness caused by the production of thick dust

**Table 4.** Physical and chemical parameter ranges for the four different cases being investigated.

	AGB	Nova	Stars of spectral Class G-K	R Cor Bor stars
[C/O]	1.5	21	1.5	7.2
Density Range ( $\text{cm}^{-3}$ )	$10^9\text{--}10^{11}$	$10^9\text{--}10^{11}$	$10^9\text{--}10^{11}$	$10^9\text{--}10^{12}$
Photosphere Temperature (K)	1500–3500	15,000–25,000	3750–6000	4500–8000
Gas Temperature (K)	1000	2000	1000	1000
Dilution Factor	see eqn (6)	$5.59 \times 10^{-5}$	see eqn (6)	$6.25 \times 10^{-4}$

**Table 5.** Table of nova parameters

Nova Parameter	30 days post-outburst
Rate of magnitude decline (optical), $\dot{m}_V$	0.03 mag d <sup>-1</sup>
Luminosity of nova, $L_{\text{nova}}$	31080
Photospheric radius, $r_{\text{phot}}$	25 $R_{\odot}$ ( $=R_{p,0}$ )
Photospheric temperature, $T_{\text{phot}}$	20,100 K

clouds (Crause et al. 2007). There are also variations in observed colour that correspond to the minimum in visual brightness and which are attributed to pulsations (Efimov 1988). These stars have fast stellar winds that feed into a thin dust shell found hundreds of stellar radii away (Walker 1986; Feast 1986). The optical properties of the ejected dust differs from the ISM, with a UV absorption peak at 2500 Å (Jeffers et al. 2012). Models indicate that this corresponds to small glassy or amorphous carbon grains (soot) formed in a hydrogen-poor environment (Hecht et al. 1984).

The dust formation mechanism is not at all well understood and there has been much debate as to where the dust condensation occurs. There are two main models: i) the first assumes the grains are formed at  $\sim 20 R_*$ , and ii) the second proposes that dust is formed in the photosphere of the star and moves quickly away due to radiation pressure (Payne-Gaposchkin 1963). The rationale behind the first method is that the stellar surface temperature greatly exceeds the grain condensation temperature for carbon (Feast 1986; Fadeyev 1988). Woitke et al. (1996) proposed that the pulsations stronger than a certain critical amplitude could cause atmospheric shocks to form in a process similar to that proposed for AGB outflows. This yields post-shock gas temperatures and densities of  $T \sim 1000\text{--}1500$  K and  $n \sim 10^8\text{--}10^9 \text{ cm}^{-3}$ , which may be propitious for dust formation. In fact, observations by Jeffers et al. (2012) indicate that there are two populations of grains which may indicate that both formation processes are occurring.

We investigate  $\text{C}_2\text{H}_2$  formation on the assumption of the first model, i.e. molecule/dust formation at a radius of  $20 R_*$  from the star. The temperature of the gas in this region is observed to be  $< 1500$  K (Goeres & Sedlmayr 1992). The effective temperature of RCB's range from 4,000–20,000 K, with mean values of 6000–8000 K for dust-forming sources (Lambert & Rao 1994). The parameter ranges adopted for this scenario are given in Table 4. The abundances for carbon, nitrogen and helium were obtained from Garcia-Hernandez et al. (2009), whereas all other abundances are assumed to be solar.

## 4 RESULTS

$\text{C}_2\text{H}_2$  formation is a necessary, but not sufficient, criterion for carbon dust formation via PAH chemistry. Therefore we need to establish the criterion for a positive result, i.e. the minimum fractional

abundance of  $\text{C}_2\text{H}_2$  that will explain the requisite abundance of dust nucleation sites. To do this, we follow Rawlings & Williams (1989); where the number of grains is equated to the number of nucleation sites. Considering the case of a nova, the number of grains,  $N_g$ , inferred from infrared observations is  $\sim 7 \times 10^{38}$  (Clayton & Wickramasinghe 1976). The dust shell condenses at a radius  $r_c \sim 8 \times 10^{14}$  cm, and has a typical thickness of  $\sim r_c/10$ . The shell volume is therefore  $V \sim 6 \times 10^{44} \text{ cm}^3$ , implying a number density of grains of  $\sim 10^{-6} \text{ cm}^{-3}$ . Note that this is a lower limit, subject to the ejecta configuration. The gas density is  $\sim 10^9 \text{ cm}^{-3}$ , hence the minimum fractional abundance of nucleation sites needed is  $10^{-15}$ . On the assumption that each  $\text{C}_2\text{H}_2$  molecule is efficiently converted into a nucleation site (i.e. that there are no kinetic bottlenecks in the formation of larger molecules), we can very crudely adopt this value as the threshold for the minimum fractional abundance of acetylene which can promote a PAH-driven dust formation pathway.

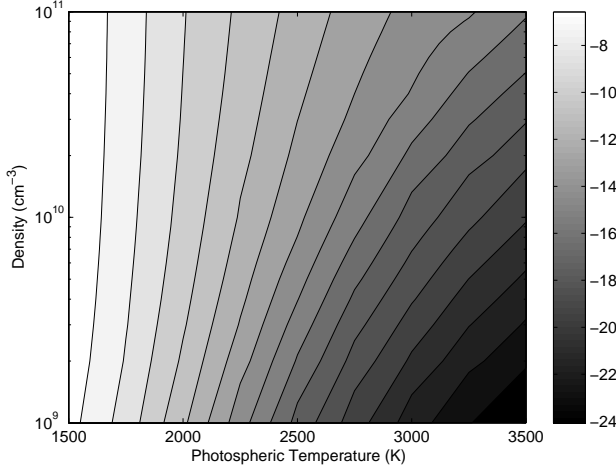
Results from our models are shown in Figures 1–4 as contour plots of the equilibrium abundance of  $\text{C}_2\text{H}_2$  as a function of density and photospheric temperature. We discuss the results for the four cases in sections §4.1 – §4.4.

### 4.1 Case I: AGB

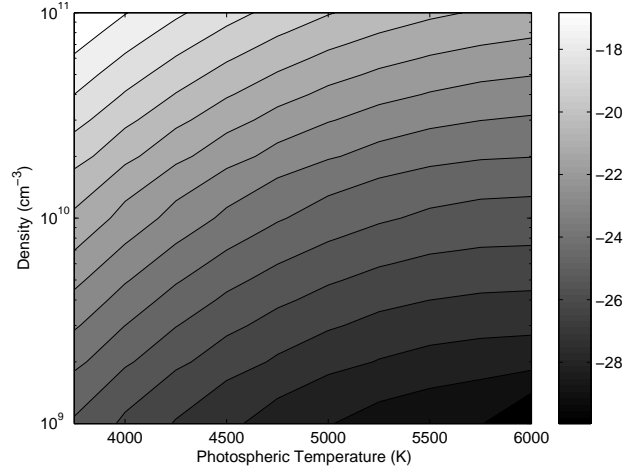
The results for AGB winds are presented in Figure 1. The figure shows that the  $\text{C}_2\text{H}_2$  abundance is not strongly sensitive to the density. There is, however, a strong dependence on the photospheric temperature. For photospheric temperatures below  $\sim 2500$  K,  $\text{C}_2\text{H}_2$  can be produced with the requisite efficiency for any density within the range explored ( $\sim 10^9\text{--}10^{11} \text{ cm}^{-3}$ ). The lack of sensitivity to density implies that if  $\text{C}_2\text{H}_2$  leads to PAH formation, then the production of dust will not be critically limited to the geometrical dilution of the wind.

### 4.2 Case II: NOVA

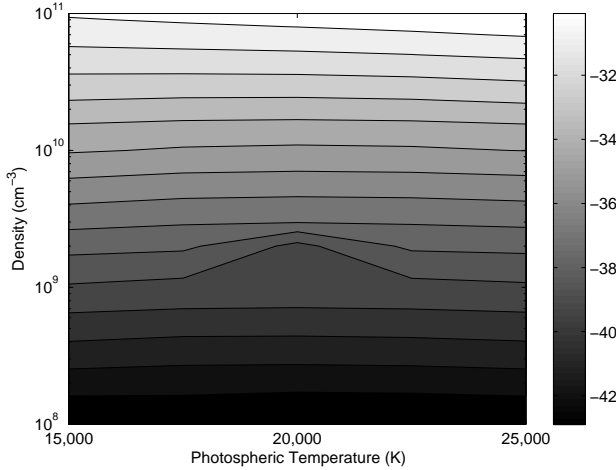
The results for nova outflows are presented in Figure 2 and show the opposite trends what was found for AGB winds; a strong dependence on density, but only a weak dependence on photospheric temperature. Despite the high abundance of carbon in novae (Starrfield, Truran & Sparks 2000), the photospheric temperatures



**Figure 1.** Contour plot showing the logarithm of the equilibrium fractional abundance of  $C_2H_2$  in the circumstellar envelope of a carbon-rich AGB star. The density and photospheric temperature are treated as free parameters. All other parameters are fixed and given values as specified in Table 4.



**Figure 3.** Contour plot showing the logarithm of the equilibrium fractional abundance of  $C_2H_2$  in the circumstellar environment of a star with spectral class G-K. The density and photospheric temperature are treated as free parameters. All other parameters are fixed and given values as specified in Table 4.

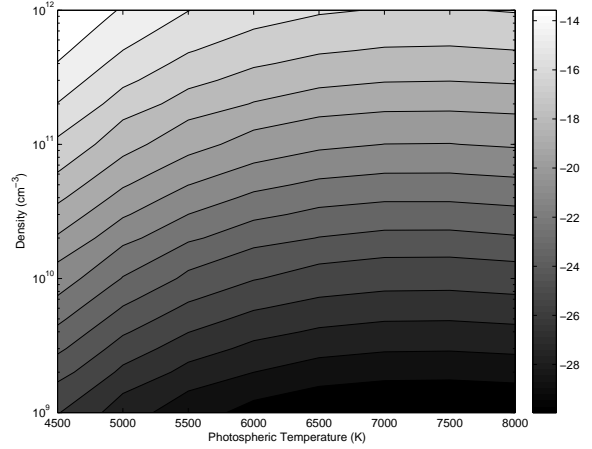


**Figure 2.** Contour plot showing the logarithm of the equilibrium fractional abundance of  $C_2H_2$  in the ejecta from a nova. The density and photospheric temperature are treated as free parameters. All other parameters are fixed and given values as specified in Table 4.

are ten times higher than for AGB stars and, even after significant geometrical dilution is taken into account,  $C_2H_2$  is highly susceptible to photodissociation and never attains appreciable abundances. This is a strongly negative result and supports the findings of previous studies (e.g. Rawlings & Williams 1989) -  $C_2H_2$  can not be produced in irradiated nova environments at abundance levels sufficient to seed dust formation via PAH chemistry. The only way that a positive result could be obtained is if the ejecta were extremely dense ( $n > 10^{13} \text{ cm}^{-3}$ ) allowing three-body chemical reactions to take place, or strongly shielded from the nova radiation field.

#### 4.3 Case III: STARS IN SPECTRAL CLASS G-K

Results for the circumstellar environment of carbon-rich stars with photospheric temperatures of 3750–6000K are presented in Fig-



**Figure 4.** Contour plot showing the logarithm of the equilibrium fractional abundance of  $C_2H_2$  in the circumstellar environment of a R Coronae Borealis star. The density and photospheric temperature are treated as free parameters. All other parameters are fixed and given values as specified in Table 4.

ure 3. The critical fractional abundance of  $C_2H_2$  is not reached. However, for the lowest photospheric temperatures ( $T < 4500 \text{ K}$ ) and highest densities ( $n > 10^{11} \text{ cm}^{-3}$ ) the abundance is very much closer to the threshold than was the case for the nova outflows. We can conclude that, whilst the spherically symmetric model produces a negative result, a positive result may be obtained in the event of ejecta clumping and/or stratification.

However, unlike the situation with AGB outflows, this result is not robust to density variations so, if the clumps were to dissipate within the temperature window for PAH formation then the  $C_2H_2$  abundance (and dust formation efficiency) would be strongly diminished.

#### 4.4 Case IV: R CORONAE BOREALIS STARS

The results for the gas in a stellar wind located at a radius of  $20 R_*$  from an R Coronae Borealis star are presented in Figure 4.

A positive result is obtained for part of the range of the physical conditions that we have investigated. The dependencies are similar to those found for the outflows from G-K stars in that there is a strong dependence on density and a weaker dependence on photospheric temperature. The requisite fractional abundance of  $C_2H_2$  is obtained for densities that  $\geq 1 - 5 \times 10^{11} \text{ cm}^{-3}$ . For photospheric temperatures  $T_{\text{phot}} < 6000 \text{ K}$ , a positive result can be obtained at lower densities. We again note that any density enhancements that may exist within the outflow will strongly strengthen this result.

## 5 CONCLUSIONS

We have used a simple model of the steady-state chemistry of several different astrophysical dust forming environments to consider the stability of acetylene ( $C_2H_2$ ). In previous studies of dust formation, based on terrestrial flame chemistries, this molecule is a precursor to PAH formation and so its presence at appreciable abundance levels can be used to establish the viability of PAH formation and, by inference, dust formation based on PAH condensation chemistry. However,  $C_2H_2$  is highly susceptible to photodissociation by stellar ultraviolet. The novel approach in this study is that we have carefully calculated the photodissociation rates for the molecular species involved in the  $C_2H_2$  chemistry, subject to the local radiation field. Previous studies had made major simplifying assumptions in this respect.

In each case we have investigated the dependence of the  $C_2H_2$  abundance as a function of gas density and photospheric temperature. In general, we find that the inclusion of accurate photorates significantly restricts the parameter space within which efficient  $C_2H_2$  formation (and hence, presumably, PAH formation) can occur.

In the case of the winds driven by thermally pulsing AGB stars, we find that - as in previous studies -  $C_2H_2$  can be formed very efficiently indeed and that a PAH chemistry is therefore at least a viable pathway for carbon dust formation in these environments. This is an interesting result as some previous studies (which have not included photochemistry in their modelling) have not been so successful at producing  $C_2H_2$  (e.g. Cherchneff, Barker & Tielens 1992; Helling et al. 1996). However, we find that this positive result only holds for photospheric temperatures that are  $< 2500 \text{ K}$ . There are dust-producing carbon AGB stars with photospheric temperatures  $\sim 3500 \text{ K}$  (e.g. Eglitis & Eglite 1995). If we were to include a more accurate physical model of the outflows, including shocks and clumping, a PAH chemistry may also be applicable in these objects. Alternatively, other dust formation mechanisms may be operating.

As compared to the dust-forming environment of AGB stars, the ejectae of novae are subject to a much stronger radiation field with a significantly higher black-body temperature. The photodissociation rates for unshielded molecular species, such as  $C_2H_2$ , are very much larger than in the other sources considered in this study (e.g. Rawlings & Williams 1989). As a result  $C_2H_2$  can never attain significant abundances. Of course, other factors should be taken into account - such as possible variations in the elemental abundances in the ejecta - but the extreme clumping required is incompatible with the observed spherical coverage of the optically thick dust shell in these objects. In this case, it seems that other (non PAH-based) formation channels must be operating -

involving species that can survive the intense radiation field (e.g.  $C_2$ , which is partly shielded by the carbon ionization continuum Rawlings & Williams (1989)).

CH subgiants have physical characteristics that are closer to Main Sequence stars than stars in the Giant phase. They have lower luminosities than equivalent stars on the Main Sequence and are known to be chemically peculiar (Smith, Coleman & Lambert 1993), having a carbon over-abundance. The winds from these stars are not expected to have the same shock-generated density enhancements as in the AGB outflows. Thus, even with the extreme parameters we have chosen, we only obtain a marginally positive result - with moderate  $C_2H_2$  abundances obtained at the lowest photospheric temperatures and highest gas densities ( $T < 4500 \text{ K}$ ,  $n > 10^{11} \text{ cm}^{-3}$ ). Again, an environment that is conducive to  $C_2H_2$ -PAH chemistry may exist if significant clumping occurs, but it would seem that alternative dust formation pathways are more likely in these environments.

Finally, we find that  $C_2H_2$  abundances that are sufficient to drive a PAH chemistry can be obtained in the winds of R Coronae Borealis stars, provided the density is high enough ( $\geq 1 - 5 \times 10^{11} \text{ cm}^{-3}$ ). This suggests that the large grains detected in the dust shells of these objects (Jeffers et al. 2012) could be produced via a  $C_2H_2$ -PAH chemistry operating in dense ejected clouds. By contrast, it is possible that the smaller grains observed in these sources may form via an alternative mechanism.

In summary, we find that  $C_2H_2$  (and PAH) formation is at least viable in AGB outflows and the denser parts of R Cor Bor winds, but is only possible in the winds of CH subgiants if significant clumping is present, and is not possible at all in nova winds. Therefore, on the basis of these studies, it is evident that the formation pathway for (carbon) dust cannot be the same in all environments; in particular, the modified flame-PAH chemistries that provide a plausible formation channel in the dust-rich winds of thermally pulsing AGB stars cannot be applied to environments such as novae and may only have a marginal importance in RCor Bor winds. It would therefore seem that multiple (and, as yet, largely undefined) pathways for the kinetic formation of carbon dust exist.

## ACKNOWLEDGEMENTS

HD acknowledges the financial support of the Science and Technology Facilities Council through a postgraduate studentship.

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